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Kinetic Studies on the Oxidation of Electrogenerated Mo(V) and Stable Monomeric Mo(V) in Sulfuric Acid Solutions

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The kinetics of polarographic catalytic reduction of nitrate and perchlorate by electrogenerated transient species of Mo(V) are investigated in 0.1M† sulfuric acid solution. Second-order rate constants for the catalytic reaction with nitrate and perchlorate obtained after Koutecky's treatment are $(2.1\pm0.4)\times10^3$ and $(1.9\pm0.1)\times10^2 M^{-1} s^{-1}$, respectively. Stable Mo(V) species in sulfuric acid solution is studied by spectrophotometry. It is concluded that there exists dimer-dimer-monomer equilibria. The oxidation of the monomer with perchlorate in 14M H_2SO_4 obeys the second-order rate law $-d[\text{monomer}]/dt=k[\text{monomer}][ClO_4^-]$, where $k=(1.59\pm0.13)\times10^{-1} M^{-1} s^{-1}$. The results indicate that electrogenerated Mo(V) in 0.1M H_2SO_4 is not the same species as the stable monomeric Mo(V) in 14M H_2SO_4.

The electrochemistry of sexivalent molybdenum ions in aqueous acidic solution has been widely investigated.[1–5] It is well known that the polarography of Mo(VI) gives catalytic waves in the presence of nitrate or perchlorate ions, and this phenomenon has been used for the quantitative analysis for Mo(VI).[3,6,7] Some conflict exists concerning the reduction mechanism of Mo(VI) and whether the catalytically active species is Mo(III) or Mo(IV).[2–5] However, recent investigations with coulometry have indicated that the catalytically active species is Mo(V).[1,8,9]

Our polarographic investigations were carried out in sulfuric acid solutions to study oxomolybdenum species. However, no quantitative investigation on the chemical equilibrium and the characteristics of Mo(V) has been reported in sulfuric acid solutions. It is not known whether the catalytically active Mo(V) species can be present as the stable species in bulk solution. The present work was carried out, (1) to obtain the rate constant for the oxidation of electrogenerated Mo(V) with nitrate or perchlorate, (2) to obtain the rate constant for the reaction of Mo(V) in bulk solution with perchlorate for comparison, and (3) to establish the equilibrium of Mo(V) in sulfuric acid solutions.

Experimental

Reagents and Apparatus. All chemicals were of reagent grade and were used without further purification. Polarographic and coulometric instruments employed in this study were the same as reported elsewhere.[10] A Hitachi 124 spectrophotometer was used for absorption measurements.

Procedure. The polarographic current values in this report were measured with RC damping, *i.e.* the average current during the drop life was measured unless otherwise noted. The catalytic current i_c was taken from the difference between the currents measured in the presence and the absence of nitrate or perchlorate at −0.36 V *vs.* SCE. The potential is 95 mV less positive than the half-wave potential of the third wave for Mo(VI) solutions without nitrate or perchlorate.[9]

The Mo(V) solutions were prepared by electrolytic reduction of $2.5—5\times10^{-3}$ M Mo(VI) in 0.1 M H_2SO_4 using a Hg-pool electrode. Oxidation of Mo(V) was initiated by mixing the Mo(V) and perchlorate solutions. Polarographic and spectrophotometric measurements were carried out at (25±0.2) °C.

Results

Polarographic Catalytic Current. Polarograms and reduction mechanisms for Mo(VI) in sulfuric acid solutions were discussed earlier.[9] There are three waves corresponding to the reduction of Mo(VI) to Mo(V) in the polarogram of 0.5 mM Mo(VI) in 0.1 M H_2SO_4. The presence of nitrate or perchlorate enhances the height of the third wave only. Figure 1 shows the relationship between the height of the third wave i_3, which should be proportional to the concentration of the species giving the third wave, and the catalytic current i_c $(=i-i_3)$. When the concentration of Mo(VI) is lower than 0.5 mM, the plot is linear. At higher concentrations, it deviates from the straight line because of the adsorptive behavior of Mo(VI) or Mo(V) at higher concentration. The current amplification by catalytic reaction depends on the concentration of the oxidant as shown in Fig. 2. The ratio of i/i_3 taken at lower concentration of Mo(VI) $(5\times10^{-5} M)$ is proportional to the square root of the concentration of nitrate or perchlorate; the second-

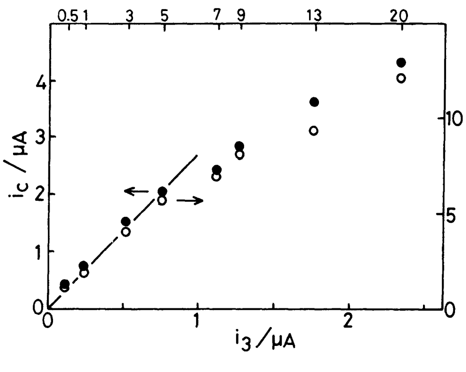

Fig. 1. Dependence of the catalytic current i_c on the height of the third wave i_3 in 0.1 M H_2SO_4: (○) with 20 mM $NaNO_3$; (●) with 50 mM $NaClO_4$.

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† 1M=1 mol dm⁻³.

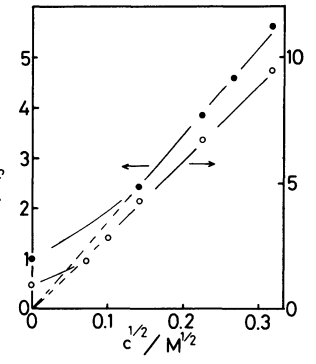


Fig. 2. Dependence of i/i_3 on the square root of the concentration of nitrate (○) and perchlorate (●). $c_{Mo(VI)}=5\times10^{-5}$M.

TABLE 1. SECOND-ORDER RATE CONSTANTS FOR THE POLAROGRAPHIC CATALYTIC REACTION IN 0.1 M H_2SO_4 $c_{Mo(VI)}=5\times10^{-5}$M

	$k_c/M^{-1}s^{-1}$
c_{NaNO_3} 5×10^{-3}—1×10^{-1}M	$(2.1\pm0.4)\times10^3$
c_{NaClO_4} 2×10^{-2}—1×10^{-1}M	$(1.9\pm0.1)\times10^2$

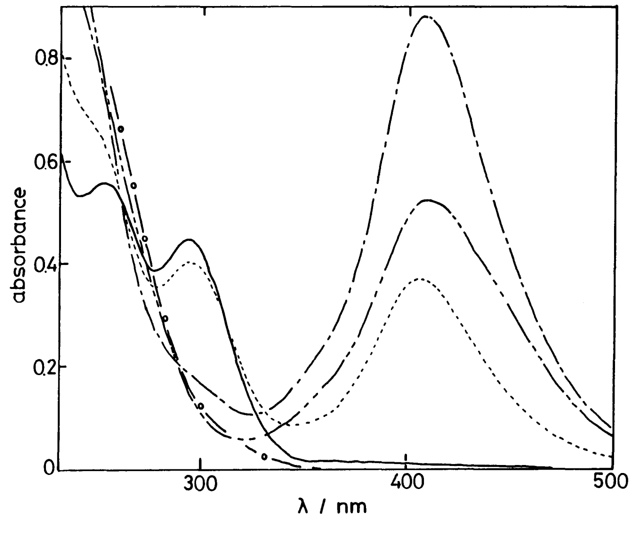


Fig. 3. Absorption spectra of 2.5×10^{-4}M Mo(V) in various concentrations of H_2SO_4: (——) 0.1 M; (------); 7 M; (— —) 9 M; (— - —) 11 M; (—・—) 15 M. l = 1 cm.

order rate constants k_c for the catalytic reduction of nitrate and perchlorate by Mo(V) are obtained by using Koutecky's treatment.[11] Results are listed in Table 1.

Absorption Spectra. Absorption spectra of 2.5×10^{-4}M Mo(V) in various concentration of sulfuric acid solution are shown in Fig. 3. In 0.1 M H_2SO_4, absorption maxima are observed at 254 nm and 293 nm. The spectrum has already been assigned to dimeric Mo(V), $Mo_2O_4^{2+}$.[12,13] When the concentration of sulfuric acid is higher than 3 M, a peak appears at 405 nm. When $c_{H_2SO_4}$ is increased to 9 M, the absorption maxima at 254 nm and 293 nm disappear, and the absorbance of the peak (407 nm) reaches its maximum and the solution looks green-yellow. In 15 M H_2SO_4, there is no absorption in the visible region. The absorbances at 254 nm, 293 nm, and 407 nm vary with $c_{H_2SO_4}$ as shown in Fig. 4. The change of absorbance at 407 nm suggests that three different species of Mo(V) are present in 0.1—15 M H_2SO_4.

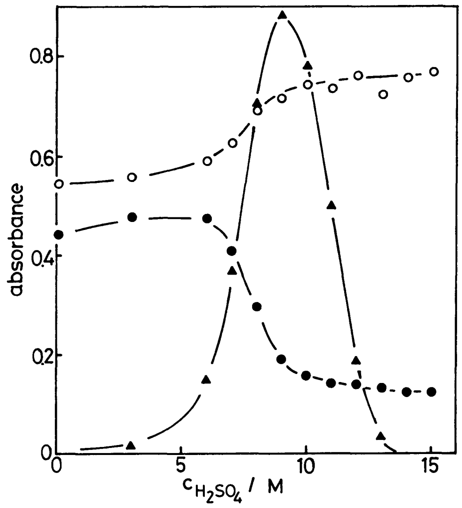


Fig. 4. Effect of the concentration of H_2SO_4 on absorbances of 2.5×10^{-4}M Mo(V) solution at 254nm (○), 293nm (●) and 407nm (▲). l = 1 cm.

Dimer-dimer-monomer Equilibria of Mo(V). In hydrochloric acid solution, dimer-dimer-monomer equilibria of chloro complexes of Mo(V) have been reported.[14,15] However, few study of such equilibria in sulfuric acid solution has been known. Marov *el al.* reported ESR investigations of Mo(V) in sulfuric acid solutions but the precise equilibrium constant could not be obtained[16,17] and no spectrophotometrical investigation of such equilibria has been known. It is well known that the predominant apecies of Mo(V) in 0.1 M H_2SO_4 is dimeric, $Mo_2O_4^{2+}$.[12,13] From the analogy of the equilibria of Mo(V) in hydrochloric acid solution, we expect that the dimer($Mo_2O_4^{2+}$)-dimer-monomer equilibria of Mo(V) in sulfuric acid solution are as follows:

$$D_1 \overset{a}{\rightleftarrows} D_2 \overset{b}{\rightleftarrows} 2M \tag{1}$$

$$K_1 = [D_2]/[D_1] \tag{2}$$

$$K_2 = [M]^2/[D_2] \tag{3}$$

$$c_t = 2[D_1] + 2[D_2] + [M] \tag{4}$$

where D_1 means the dimer, $Mo_2O_4^{2+}$, D_2 the other dimer and M is a monomer; K_1 and K_2 are the equilibrium constants and c_t is the total concentration of Mo(V). Spectrophotometric data were treated with Haight's procedure.[14] When $c_{H_2SO_4}$ is lower than 9M, equilibrium a in Eq. 1 should predominate. From the result of Fig. 3 we conclude that only the species of D_2 absorbs at 407 nm; therefore the absorption at 407 nm is,

$$A_{407} = \varepsilon_2[D_2] \tag{5}$$

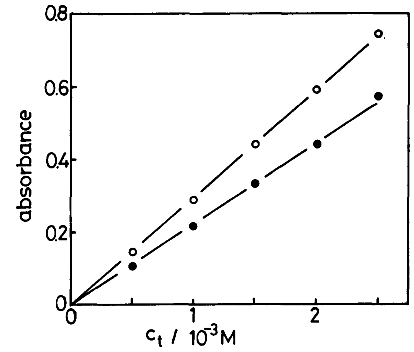


Fig. 5. Dependence of A_{407} on c_t in 7.5 M (●) and 8 M (○) H_2SO_4.

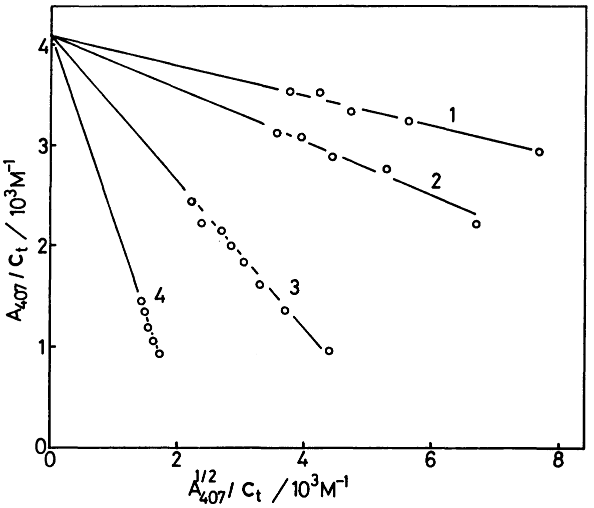


Fig. 6. Dependence of A_{407}/c_t on $A_{407}^{1/2}/c_t$ in H_2SO_4. $c_{H_2SO_4}$: (1) 9 M; (2) 10 M; (3) 11 M; (4) 12 M.

where ε_2 is the molar absorptivity of D_2. Equation 6 follows from Eqs. 2, 4 ([M]=0) and 5.

$$A_{407} = \varepsilon_2 K_1 c_t/2(1+K_1) \tag{6}$$

Therefore, if K_1 is a constant which is independent of c_t, A_{407} should be proportional to c_t when $c_{H_2SO_4}$ is lower than 9 M. The dependence of A_{407} on c_t in 7.5 M and 8 M H_2SO_4 shown in Fig. 5 indicates that D_2 is dimeric.

When $c_{H_2SO_4}$ is higher than 9 M, equilibrium b in Eq. 1 should predominate. In this case,

$$c_t = 2[D_2] + [M] \tag{7}$$

and from Eqs. 3, 5, and 7, we obtain

$$A_{407}/c_t = \varepsilon_2/2 - (\varepsilon_2 K_2/4)^{1/2} A_{407}{}^{1/2}/c_t. \tag{8}$$

A plot of A_{407}/c_t *vs.* $A_{407}^{1/2}/c_t$ (Fig. 6) gives a straight line with slope $-(\varepsilon_2 K_2/4)^{1/2}$ and intercept of $\varepsilon_2/2$. From the average value of ε_2 (8.17×10^3 $M^{-1}cm^{-1}$) obtained, K_1 and K_2 were calculated for various $c_{H_2SO_4}$ and are listed in Table 2. When $c_{H_2SO_4}$ is higher than 13 M, monomeric Mo(V) is a predominant species.

Table 2. Equilibrium constants for dimer(D_1)-dimer(D_2)(K_1) and dimer(D_2)-monomer (M)(K_2) in various concentration of H_2SO_4

$c_{H_2SO_4}$/M	K_1	$c_{H_2SO_4}$/M	K_2/M
3	1.80×10^{-2}	9	1.17×10^{-5}
6	1.71×10^{-1}	10	3.97×10^{-5}
7	5.71×10^{-1}	11	2.28×10^{-4}
7.5	1.28	12	1.71×10^{-3}
8	2.24		

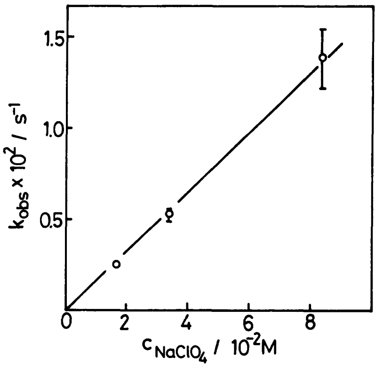


Fig. 7. Dependence of k_{obsd} on the concentration of perchlorate.

Oxidation of Monomeric Mo(V) by Perchlorate. The oxidation rate of monomeric Mo(V) by perchlorate was studied by conventional spectrophotometry in the presence of excess perchlorate in 14 M H_2SO_4. The decrease in absorption at 260 nm was used to monitor the reaction. Absorbance at 260nm, A_{260}, is given by

$$A_{260} = \varepsilon_M[M] + \varepsilon_{VI}[Mo(VI)], \tag{9}$$

where ε_M and ε_{VI} are the molar absorptivities of M and Mo(VI), respectively. [M] is given by

$$[M] = (A_{260} - \varepsilon_{VI}c)/(\varepsilon_M - \varepsilon_{VI}), \tag{10}$$

where $c = [M]+[Mo(VI)]$. A plot of ln[M] *vs.* time was linear to >90% completion. The pseudo-first-order rate constant determined from the plot was linearly dependent on the concentration of perchlorate as shown in Fig. 7. Therefore, the rate law is expressed as

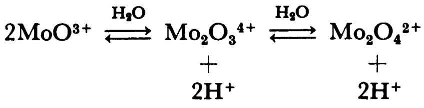
$$-d[M]/dt = k_{obsd}[M] = k[M][ClO_4^-], \tag{11}$$

where k is the second-order rate constant for oxidation of monomeric Mo(V) by perchlorate. The value for k (1.67×10^{-2}–8.33×10^{-2} M perchlorate) was $(1.59 \pm 0.13) \times 10^{-1} M^{-1} s^{-1}$ in 14 M H_2SO_4. The corresponding oxidation by nitrate could not be studied because of the large absorbance of nitrate in the UV region. Oxidation of $Mo_2O_4^{2+}$ by perchlorate is extremely slow[18] and that of the dimer in 9 M H_2SO_4 can not be monitored precisely because the monomer is involved simultaneously. The approximate rate constant obtained is about 1000 times smaller in 9 M H_2SO_4 than in 14 M H_2SO_4.

Discussion

Recent coulometric investigations in the presence of nitrate and perchlorate have indicated that the catalytically active species is Mo(V).[1,8,9] Paffett and Anson suggested that monomeric Mo(V), $[MoO(OH)(H_2O)_4]^{2+}$, is the catalytically active species,[1] but they did not study the kinetics of the catalytic reaction. Our data on kinetics for the catalytic reaction based on Koutecky's procedure (Table 1) might be compared with data for oxidation of monomeric Mo(V) in bulk solution. However, since such experiments have involved the presence of added ligands which form complexes with Mo(V)[17] or referred to dimeric Mo(V),[18] the direct comparison is not straightforward.

A chloromolybdenum(V) complex in hydrochloric acid solution is involved in dimer-dimer-monomer equilibria.[14,15] In the absence of other complexing ligands, the following equilibria have been considered.



$$2MoO^{3+} \underset{}{\overset{H_2O}{\rightleftharpoons}} \underset{2H^+}{\underset{+}{Mo_2O_3^{4+}}} \overset{H_2O}{\rightleftharpoons} \underset{2H^+}{\underset{+}{Mo_2O_4^{2+}}}$$

However, no quantitative experiment has been performed.[20] The existence of dimer-dimer-monomer equilibria of Mo(V) is indicated in the present work for sulfuric acid solution. It is not known whether monomeric Mo(V) in 14 M H_2SO_4 is MoO^{3+}. The existence of sulfato complex of monomeric Mo(V), $MoO(HSO_4)_5^{2-}$, has been considered,[16,17] but, detailed structural information can not be obtained at the present stage.

The rate of the reaction involving perchlorate should increase with the activity of hydrogen ion, though the second-order rate constant for oxidation of monomeric Mo(V) with perchlorate in 14 M H_2SO_4 is found to be about 1000 times smaller than that for the reaction of electrogenerated Mo(V) with perchlorate in 0.1 M H_2SO_4 (5×10^{-5}—5×10^{-4}M Mo(VI)). Therefore, monomeric Mo(V) in 14 M H_2SO_4 is not the same species as electrogenerated Mo(V) in 0.1 M H_2SO_4. It has been proposed that a monomeric cation of Mo(V), $[MoO(OH)(H_2O)_4]^{2+}$, is the catalytically active species,[1,10] and this electrogenerated monomer is more reactive than the monomer in bulk solution.

Lahr *et al.* suggested that participation of the MoO^{3+} center might be widespread in catalytic reactions of Mo(V) in aqueous media.[21] In sulfuric acid solutions, both electrogenerated Mo(V) in 0.1 M H_2SO_4 and monomeric Mo(V) in 14 M H_2SO_4 seem to have the MoO^{3+} center, and their oxidation rates with perchlorate are quite different. Thus, other structural characteristic of the catalytically active species of molybdenum having the MoO^{3+} center remains to be established.

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